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Effect of Tannin on Flexural Properties of Phenol Formaldehyde Glycerol Reinforced Composites: Preliminary Results

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Abstract: Phenol formaldehyde composites are modified with glycerol/tannin mixes with varying percentage by weight of phenolic resin to glycerol/tannin. The glycerol to tannin ratio is also varied. In this work also different percentages by weight of SLG (a commercial ceramic microsphere) are added to the composites. The effect of glycerol/tannin mix and added SLG on the flexural properties was studied. It was found that the flexural stress decreases gradually with increasing tannin when there is no SLG. With SLG, the presence of tannin in the composites reduces the flexural stress drastically. Tannin reduces the strain at break. With SLG, this reduction of the yield strain is more apparent. Tannin increases the flexural modulus of the composite and SLG acts in the opposite direction. The use of tannin in the phenolic composites improves the 'green' character of the composite materials. It was also found that the presence of tannin made the mixing of phenolic resins with glycerol easier.

Keywords: Phenolic resin, phenol formaldehyde, tannin, glycerol, SLG, flexural strength, strain at break and flexural modulus**.**

1. Introduction

A research centre in University of Southern Queensland (USQ) has begun work in recent years to develop novel thermosetting resin toughening agents based on bio-based sources. These additives have shown great promise to date, being simultaneously inexpensive, highly-effective and environmentally beneficial. One leading candidate for the toughening of phenolic resins is bio-based tannins, containing natural phenol chemical functionalities which have been identified to be of particular interest for its 'green' character, its readily availability in the market and its low cost.

In this research project, the study was based on the development of phenolic and biodegradable additives composites with tannin obtained from different trees. Preliminary research work has shown that these tannin additives can be successfully incorporated into commercial resole phenolic resins. However, remains many unanswered technical questions regarding the addition of these additives, especially in terms of the mechanical performance of civil engineering composites manufactured using these biodegradable type of plasticizer additives. This study consisted of evaluating the flexural properties and the influence of different proportions of tannin mixed with glycerol and SLG in phenolic composites.

Samples have been made with a view to understanding the behaviour and the influence of different proportions of tannin and SLG in bio-based tannins phenolic composites. Each sample is based on the weight of 100g that correspond to the mass of phenolic resin plus the mass of a mixture composed of glycerol (plasticizer) and tannin. After that, some SLG will be added. Five different types of mixture have been made and they are: mixture A (100 % Glycerol and 0% Tannin); mixture B (90% Glycerol and 10% Tannin); mixture C (80% Glycerol and 20% Tannin); mixture D (70% Glycerol and 30% Tannin) and mixture E (60% Glycerol and 40% Tannin). When SLG was used it was necessary to add a thixotropic agent (powder Aerosil) to allow the proper dispersal of the SLG in the phenolic matrix. In 100 g of the resin and the glycerol/tannin mix (mixtures A to E), samples with 0, 20 and 30 g of SLG were prepared.

Three-point bending tests are carried out to evaluate the flexural properties (flexural stress, strain at break and flexural modulus) of the material. The samples made with Mixture C are tabulated as in Table 1. Phencat 15 is the catalyst used for the reaction. It is just necessary to

change the mixture and keep the same proportions of the other constituents to obtain the 80 samples.

2. Materials

2.1 Phenol formaldehyde and its catalyst

The commercial resole resin used in this study was J-2027L produced by Borden Ltd. Its official name is Borden Cellobond J2027L [1]. The acid catalyst used to crosslink the resin was Phencat 15, which is a fast action acid catalyst. Its composition is shown in Table 2. There is a strong exothermic reaction when phenolic resin is mixed with catalyst. The ratio by weight of the resin to hardener for all samples in this work was chosen to be 50: 1. The phenolic Borden Cellobond J2027L is as a brown viscous liquid with a characteristic phenolic smell. Using the resin it is necessary to wear a mask as the gas emissions from the resin are noxious. This resin it is more commonly called resole phenolic resin [2].

Table 3 shows the composition of Borden Cellobond J2027L. It is composed from the reaction of phenol and formaldehyde; these two chemicals products react to form a hydroxymethyl derivatives phenol, but the reaction is incomplete and therefore there is a remaining of unreacted formaldehyde and phenol and also water that evolves during the condensation reaction between phenol and formaldehyde.

With reference to phenolic molecule of Figure 1, there are five 5 hydrogen atoms in the benzene ring but because of limited space, there are only three possible sites for reaction and the phenolic molecule is said to have a functionality of three [3, 4]. As the functionality of

the phenolic molecules is greater than two, the molecules can react with formaldehyde molecules to form 3-D network polymer [5].

2.2 Biodiesel Glycerol

Biodiesel glycerol is a plasticizer agent for phenolic resins and is obtained as a sub-product from the production of biodiesel using common vegetable oils. As a plasticizer agent when added to phenolic composites it increases the elasticity and toughness of the phenolic materials. This is because the presence of glycerol in the phenolic network reduces the characteristic brittleness of phenolic resins by decreasing the crosslink density of the cured composites.

2.3 The bio-based tannin (Bondtite 345)

It is wattle tannin and is supplied by Bondtite Co. Ltd in Australia. This tannin is a dark brown powder which contains moisture of less than 10%. Tannin is an excellent renewable resource for replacing petroleum derived phenolic compounds. The major wood species from which it can obtained are mimosa, quebracho and radiata pine. The structure of the main polymeric constituents of wattle tannin can be represented in Figure 2. Because of their size and shape, the tannin molecules become immobile at a low level of condensation with formaldehyde and the available reactive sites are too far apart for further methylene bridge formation. The result is incomplete polymerization and therefore weakness. Bridging agents with longer molecules, such as phenol/formaldehyde condensates, have been shown capable of bridging the distances that are too large for methylene bridges [6].

2.4 E-spheres, SLG

Envirospheres SLG (E-spheres) is a commercial ceramic microsphere product obtained as a fly ash by-product. The particle size of this general purpose E-spheres ranges from 20 – 300 µm with approximate mean of 130 µm. The relative density of E-spheres is 0.7. E-spheres are a combination of Silica, SiO_2 (55-60%), Alumina, Al_2O_3 (36-44%), Iron Oxide, Fe_2O_3 (0.4-0.5%) and Titanium Dioxide, TiO_2 (1.4-1.6%).

2.5 Aerosil COK 84

It is a white powder which is based on a mix of hydrophilic fumed silica and highly dispersed fumed aluminium oxide in the ratio of 5:1. Normally, Aerosil is applied as a thixotropic agent in liquid systems to improve their rheological properties. In this study, it facilitates the homogeneous dispersal of SLG in the samples.

3. Sample preparation

3.1. Mixture of glycerol and tannin

Five different mixes (A to E, as mentioned above) were made in this study. For each mix, 700g were prepared. In order to facilitate the mixture between the glycerol and the tannin, 1 g of sulphuric acid was added (except for Mix A) for each 100 g of mixture. The proportions of the mix are shown in Table 4. To prepare the mix, the glycerol and sulphuric acid were mixed at a temperature between 80-100°C. After that, the tannin was carefully added to the mixture of glycerol and sulphuric acid; the mixture was stirred until there was no more tannin

left; stirring was continued for the next 45-60 minutes. The higher the content of tanning the higher was the viscosity of the mix.

3.2. The samples

Each sample has been prepared in a round plastic container (diameter: 9cm, height: ≈8cm) and all samples have the same protocol of preparation; first, the phenolic resin was put into the container, then, the glycerol/tannin mixture was added followed by stirring the two liquid components until the mix was homogeneous (usually after 3 to 5 minutes of stirring the mix). After that, there were two cases of dealing with samples:

- If there was not SLG, the catalyst was added to the mixture of the two liquids and then they were mixed quickly for 3 or 4 minutes.
- If there was SLG, the E-spheres and the Aerosil were added to the mixture of the two liquids and they were then mixed until a homogeneous mixture was observed (3 to 5 minutes); after this, the catalyst was added and further mixed quickly for additional 3 to 4 minutes.

The quantity of Aerosil added depended on the SLG added. With more SLG, e.g. 40g, more Aerosil, e.g. 2g, had to be added in order to have a good dispersal of the SLG in the sample. For 20g and 30g of SLG, 1g of Aerosil was enough. The samples were initially left to cure at room temperature for overnight. The more tannin in the sample, the more catalyst had to be added.

3.3. Post curing the samples

After curing the samples for overnight at ambient conditions, the samples were post-cured in an oven for 4 hours at 80°C. Any traces of water left behind would be driven out by this curing process. It is important to add enough quantity of catalyst to the samples to harden them before putting in the oven; if insufficient quantity of catalyst had been added, the samples would still be soft even after they were cured in ambient conditions for one night. On the other hand, if excessive catalyst had been added, the curing would be fast, highly exothermic and bubbles would evolve, resulting in unusable material.

3.4 Samples and testing

When a sample was taken out of the plastic container, the sample has a round shape and a height depending on the quantity of SLG. The height ranges from between 1cm (without SLG) to 2.5 cm (with 40g of SLG). In order to obtain a sample which can be used for flexural strength analysis, it is necessary to cut them to the required dimensions.

With the circular saw, 4 or 5 test samples were cut to the same thickness. The standard used for the mechanical test is ISO 14125:1998(E), which allows the results to be compared with the published literature of similar polymeric materials [7]. A Material Testing Systems (MTS) 810 was used for the tests and the software used was TESTWORKS 4. The dimensions of the specimens of resins were 100mm x 10mm x 4mm and tested at a crosshead speed of 1 mm/min.

4. Results and discussion

Three point bending tests were used to evaluate the flexural properties of the composites [8]. As mentioned, the tests were carried out in accordance with ISO 14125:1998(E). The results will presented in three different parts, flexural stress, strain at break and flexural modulus.

4.1 Effect of glycerol/tannin on flexural strength

Figure 3 shows the flexural strength of phenolic composites without SLG. The values of the flexural strength of composites with no tannin were higher than their counterparts. However, the difference in values of the flexural strength of composites with Mixture A (0 % of Tannin) and B (with 10 % of Tannin) was minimal. Those values of composites with Mixture B were within the 5 percent markers of the values of composite with Mixture A. However, the values the flexural stress of the composites with Mixture E (40% tannin) were at least 24 % lower than those with Mixture A; this indicates that the glycerol plays a significant role as a plasticiser agent inside of the phenolic network, while the increasing addition of tannin mixed with Glycerol clearly has the opposite effect to glycerol on the flexural strength of the phenolic network.

The results indicate that the presence of tannin decreased the flexural strength of the composites. The peak flexural strength of composites with Mixture A was 49 MPa when the percentage by weight of the mixture was 21.5 %. The peak flexural strength of composites with Mixture B was 47 MPa when the percentage by weight of the mixture was 26 %. The peak flexural strength of composites with Mixture E was 26 MPa when the percentage by weight of the mixture was 31.5 %. Clearly, as the amount of Tannin mixed with Glycerol increased and also the amount of the glycerol/tannin in the phenolic resin increased, there is a continuous decrease in the flexural strength of the composites.

Figure 4 shows the flexural strength of phenolic composites with 20% by weight of SLG. It is evident that the values of flexural strength are much lower than their counterpart in Figure 3. This is totally due to the presence of SLG in the mixtures as previously reported [9]. In addition, the values also dropped linearly with increasing percentage by weight of mixtures in the samples; this applies to all Mixtures (A, to E). The decreasing trend was even larger with composites with Mixture A (no tannin). Up to 30% by weight of mixtures, the values of flexural strength of the materials with Mixture B and Mixture E were within 5 percent markers of those with Mixture A as depicted in Figure 4; clearly, in the composites with SLG filler the increasing addition of tannin to the glycerol/tannin mix appears to improves the flexural strength of the composites. This effect may be due to an improvement of the interface interaction between the SLG filler and the phenolic matrix by the added tannin. However, further work it is required to fully clarify this effect of tannin in the composites.

It should be noted that the addition of SLG reduced the flexural strength of the composite drastically; the peak flexural stress of composite with Mixture B and 0 % SLG was 45.8 MPa while the strength of the equivalent sample with 20% of SLG was 9.1 MPa; the drop correspond to about 80% of the initial value. This indicates that SLG acts a filler inside of the resin matrix, not as a reinforcing agent, and therefore the purpose of adding SLG to the composites is to reduces the overall cost (SLG is quite cheap in comparison with the cost of the resin), but there is a proportional decreases in the mechanical performance of the materials with increasing SLG content. Also the results indicate that this negative effect of SLG on the mechanical properties of the composites can be partially compensated by the addition of tannin dissolved in glycerol to the composites.

Figure 5 shows the flexural strength of phenolic composites with glycerol/tannin with 30% SLG; it was observed that the flexural strength decreased slightly with increasing mixture by weight; the decreasing trend was more significant for the composites with Mixture A (no tannin), similarly to the samples with 20% SLG content, as shown in Figure 4. The increases in SLG further reduced the flexural strength of the composites; the peak flexural strength of composites with 30% of SLG and Mixture E was 10.5 MPa, while that with 20% of SLG and the same mixture was 15.08 MPa; this is a drop of 30%. The increase of tannin content in the composites samples with 30% SLG content resulted in a proportional increases of the flexural strength as shown in Figure 5, this confirms that the increasing presence of tannin in the network of the composites with SLG increases the flexural strength of the materials.

4.2 Effect of glycerol/tannin on strain at break (%)

Figure 6 shows the strain at break (%) of phenolic composite reinforced with glycerol/tannin with 0% (without) SLG; it can be found that the strain at break increased with the amount of glycerol/tannin added to the phenolic resin and peaked at some point before dropping back when the tannin by weight was over 30%. The composite with Mixture A was used as a reference and its strain at break peaked at 3.8% when Mixture A was 31.5 % by weight; the results confirm that the increasing addition of glycerol resulted in a proportional increases of the strain at break up to 30% addition to the resin, but above this value there is a decreases in the strain at break values with further addition of glycerol. Therefore, for composites without SLG, the presence of glycerol/tannin in the phenolic network increased the flexural strength and the strain at break, which as previously mentioned is due to the toughening effect of the glycerol/tannin inside of the cured phenolic network. With added SLG filler (see Figures 7 and 8) there is an initial increase in the values of the strain at break with increasing glycerol

and glycerol/tannin mix up to 20%. However, further increases in the amounts of glycerol/tannin decrease the strain at break of the composites; with the Mixture E (40% tannin) the strain at break was at least 66 % lower than those with Mixture A This effect was quite similar to that of the glycerol/tannin mix on the flexural stress values of the composites. Therefore, the results clearly indicate that in the absence of SLG filler, the increasing amount of tannin in the mix with glycerol in the composites reduces the flexural strength and flexural strain of the materials. However, with added SLG filler the effect of tannin in the mechanical properties is more complicated; the strain at break initially increased with the amount of tannin but the strain at break decreased with increasing glycerol/tannin when the amount of the mix in the composites was above the 20% mark, as shown in Figures 7 and 8. It should be also mentioned that the addition of SLG filler reduced the strain at break in comparison with the samples without SLG, similarly to the above reported results of the flexural strength of the composites.

Figure 8 shows the strain at break (%) of phenolic composite reinforced with glycerol/tannin with 30% SLG; similarly to the results presented in Figure 7 for the samples with 20% SLG, it was found that the strain at break increased slightly with increasing percentage by weight of mixture and peaked at some point before dropping back when the mixture by weight was over 25%. This confirms that the increases in SLG filler results in a proportional decreases in the strain at break of the composites. The increasing amount of tannin in the mix with glycerol resulted in even lower values of the strain at break as depicted in Figures 7 and 8.

4.3 Effect of glycerol/tannin on flexural modulus

Figure 9 shows the flexural modulus of phenolic composite reinforced with glycerol/tannin with 0 % SLG; it can be found that the flexural modulus decreased with increasing percentage

by weight of the mixture. Without SLG, the flexural modulus at 40 % be weight of Mixture A was only 1.05 GPa; with 30 % by weight of SLG, its value was 1.78 GPa; an increase of 70 %. The lowest flexural modulus was found in composite with Mixture A and percentage by weight of mixture of 40 %; its value was 1.025 GPa. Therefore, it is evident that with an increase in the glycerol content in the composites there is a proportional decrease of the flexural modulus, but with an increase in the amount of tannin dissolved in glycerol in the composite formulation there is an increases of the flexural modulus in comparison with the composites without tannin. This can be explained in terms of the effect of tannin on the interface between the SLG filler and the phenolic resin, where the tannin appears to improve this interaction between the filler and the matrix [10].

Figure 10 shows the flexural modulus of phenolic composites reinforced with glycerol/tannin and with 20 % SLG; it was found that the flexural modulus decreased with increasing percentage by weight of the mixture. With 20 % SLG, the values of the flexural modulus continuously decreased irrespective of the percentage by weight of the mixture. The lowest value of the flexural modulus was found in the composites with Mixture A and percentage by weight of the tannin/glycerol mixture of 40 %; however, the increases of tannin in the composites formulation resulted in an proportional increases in the flexural modulus, similarly to the results without SLG, as shown in Figure 9.

Figure 11 shows the flexural modulus of phenolic composites reinforced with glycerol/tannin and with 30 % SLG; it can be observed that the flexural modulus decreased with increasing percentage by weight of the mixture. With 30 % SLG, the values of the flexural modulus were lower than the values of the composites with only 20% of SLG (see Figure 10) or without SLG (see Figure 9). Similarly to the previous results, the increases in tannin dissolved

in glycerol resulted in a proportional increases in the flexural modulus of the composites. Considering the overall mechanical performance of the composites with only glycerol/tannin and without SLG filler (Figures 3, 6 and 9), there is a decreases in the flexural strength and flexural strain with increasing tannin content, but the results showed the opposite behaviour for the flexural modulus where there is an increases with the amount of tannin dissolved in This is not surprising as the values of flexural modulus are obtained by dividing the flexural stress by the flexural strain. It can be argued that the trend even including flexural modulus was consistent and the values of the flexural stress, strain and modulus are therefore reliable. With the presence of 20% of added SLG (Figures 4, 7 and 10), the trend is quite similar to the samples without the filler, except for the flexural strength that clearly decreased as the amount of glycerol/tannin mixture increased. For the values of the samples with higher SLG content (30%, see Figures 5, 8 and 11) the behaviour of the mechanical properties is more complicated with the flexural modulus decreasing as the glycerol/tannin mixture increased, but the flexural strength and flexural strain observed a higher variability in their values. However, there is a defined increase in the flexural strength as the amount of dissolved tannin in the composites increased, which is accompanied with a decreases in the flexural strain for the same samples. Moreover, tannin can also partially replace the phenol in phenol-formaldehyde resin as reported by other researchers [11 – 13]. This is critical as petroleum crisis is surging again in our time.

5. Conclusions

Without SLG filler in the composites, the flexural strength reach a maximum of 20 % to 25 % of added glycerol/tannin mixture, but further increase is followed by a decrease in the flexural strength of the composites. Also there is a decrease in the flexural strength with increasing

amount of tannin in the formulations. With SLG filler in the composites, the increasing amount of glycerol resulted in a decrease of the flexural strength, but this effect was compensated as the amount of dissolved tannin increased in the composites formulations.

The increase of tannin in the composites was also accompanied with a decrease in the flexural strain at break, with and without SLG, which indicates a molecular interaction (crosslinking) between the tannin and the phenolic resin. As a result of this molecular interaction between tannin and phenolic, the flexural modulus increased with higher tannin content in the composites. Finally, the use of tannin (a renewable and a biodegradable additive) as a toughening agent in phenolic composites increases the 'green' character of the materials, making them more attractive as a structural material in future civil engineering applications. This is particularly true when tannin is used to partially replace the phenol in phenol-formaldehyde resin [11, 12].

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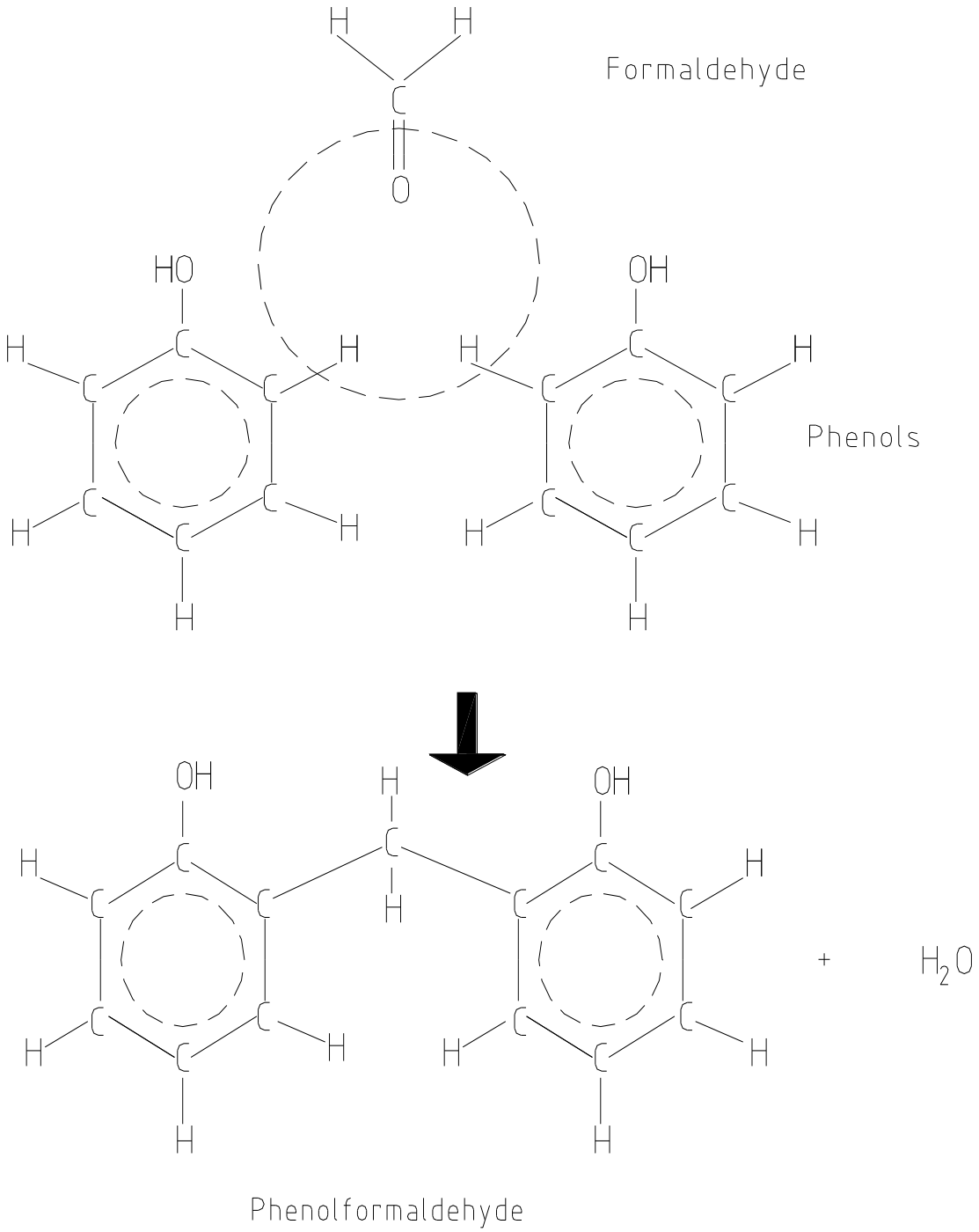

Figure 1: Formation of Phenol formaldehyde

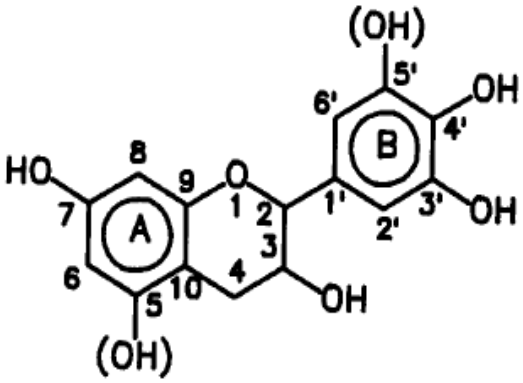

Figure 2: Structure of wattle tannin

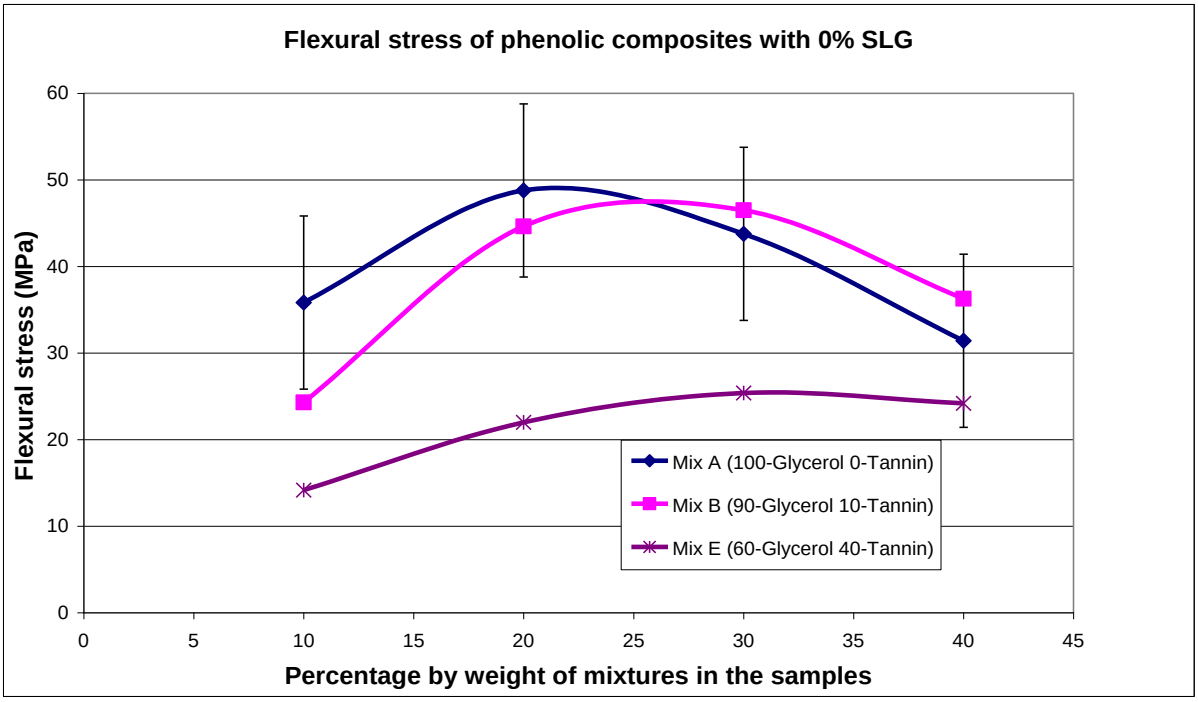

Figure 3: Flexural stress of phenolic composite with 0% SLG

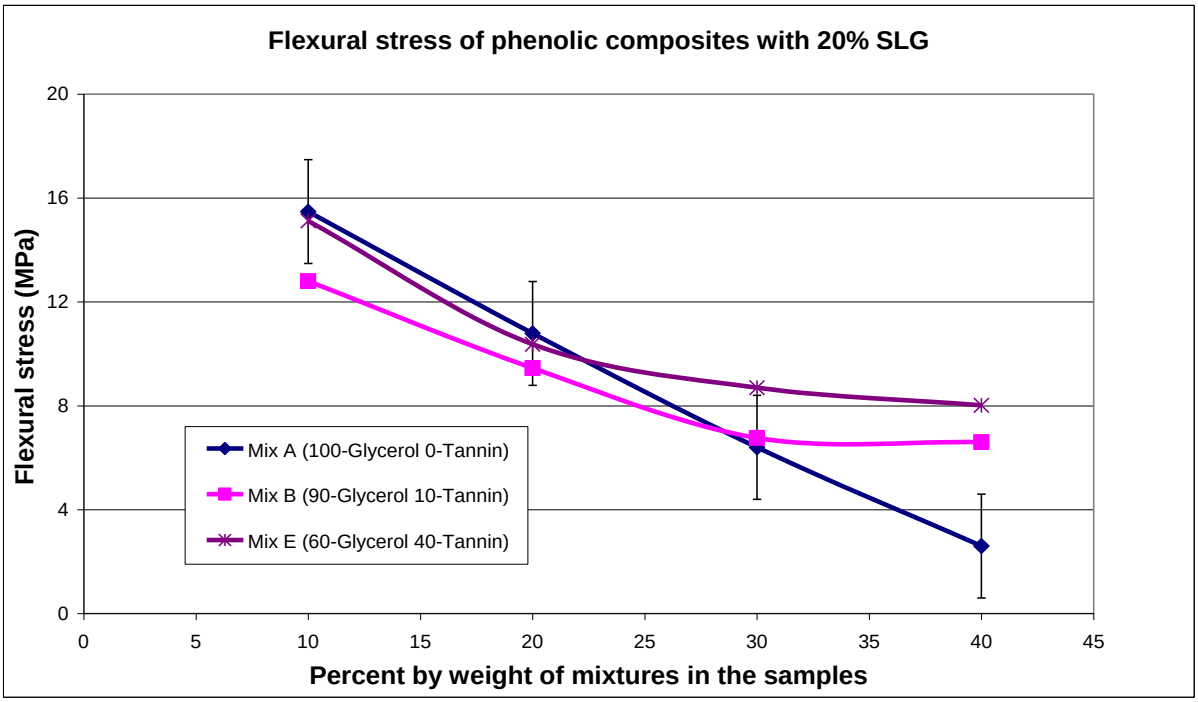

Figure 4: Flexural stress of phenolic composite with 20% SLG

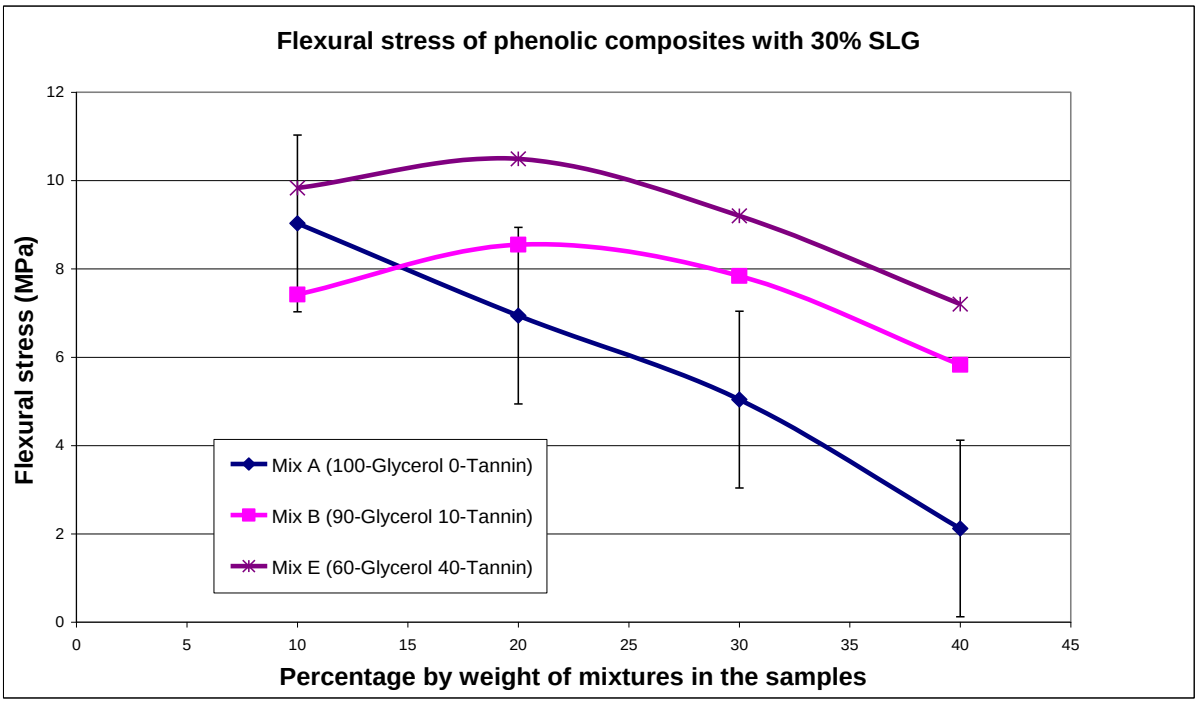

Figure 5: Flexural stress of phenolic composite with 30% SLG

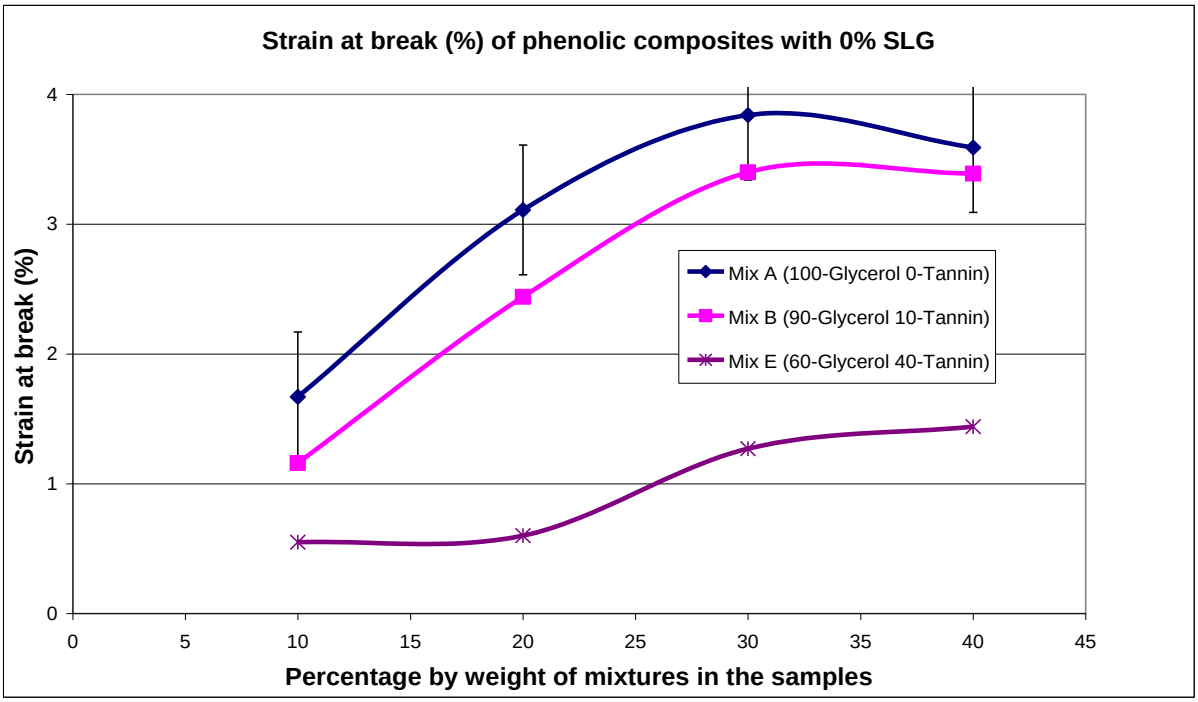

Figure 6: Strain at break (%) of phenolic composite with 0% SLG

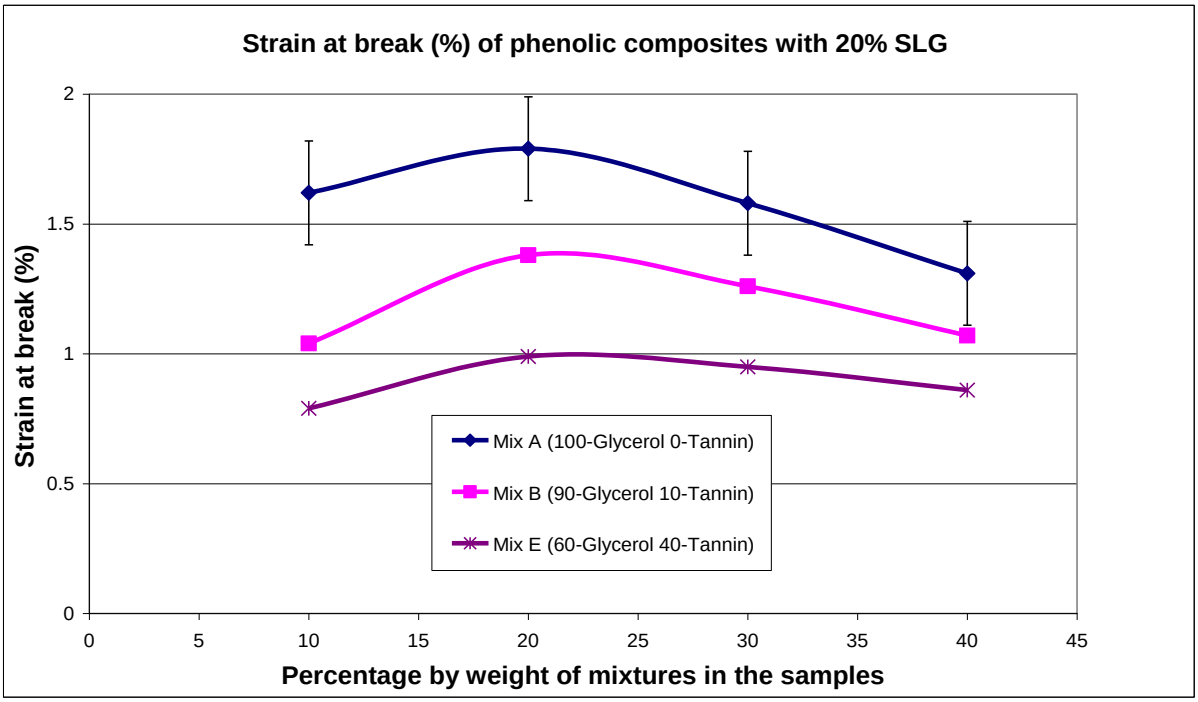

Figure 7: Strain at break (%) of phenolic composite with 20% SLG

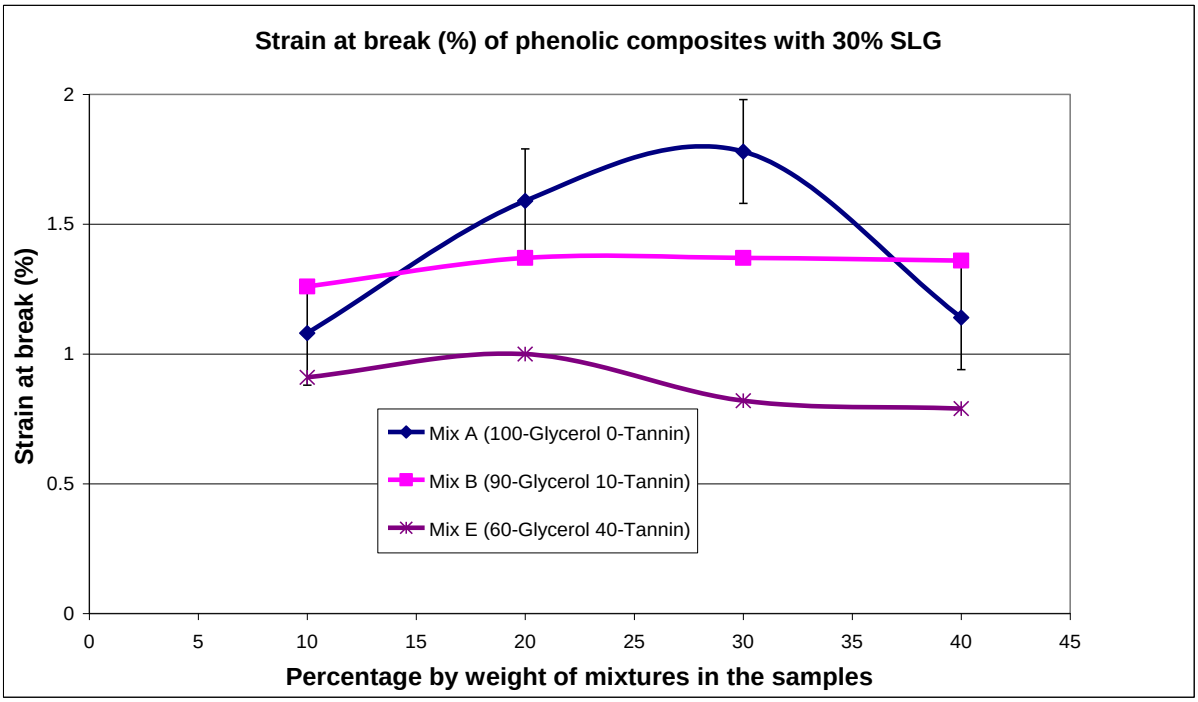

Figure 8: Strain at break (%) of phenolic composite with 30% SLG

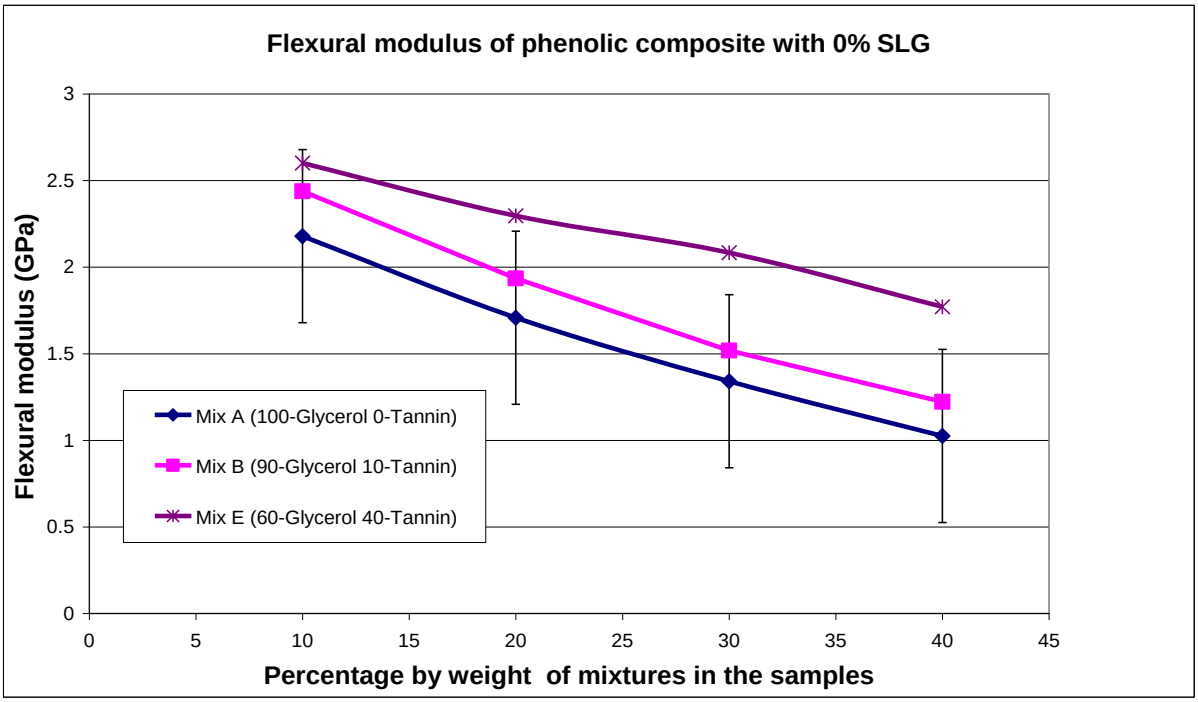

Figure 9: Flexural modulus of phenolic composite with 0% SLG

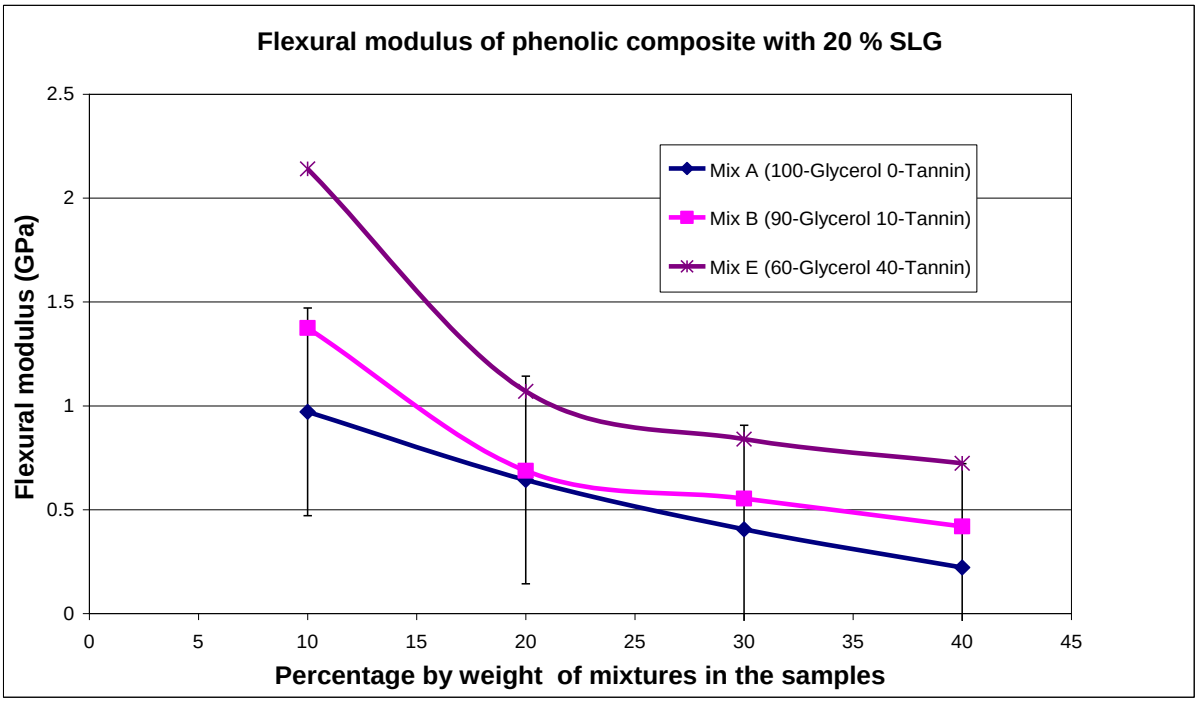

Figure 10: Flexural modulus of phenolic composite with 20% SLG

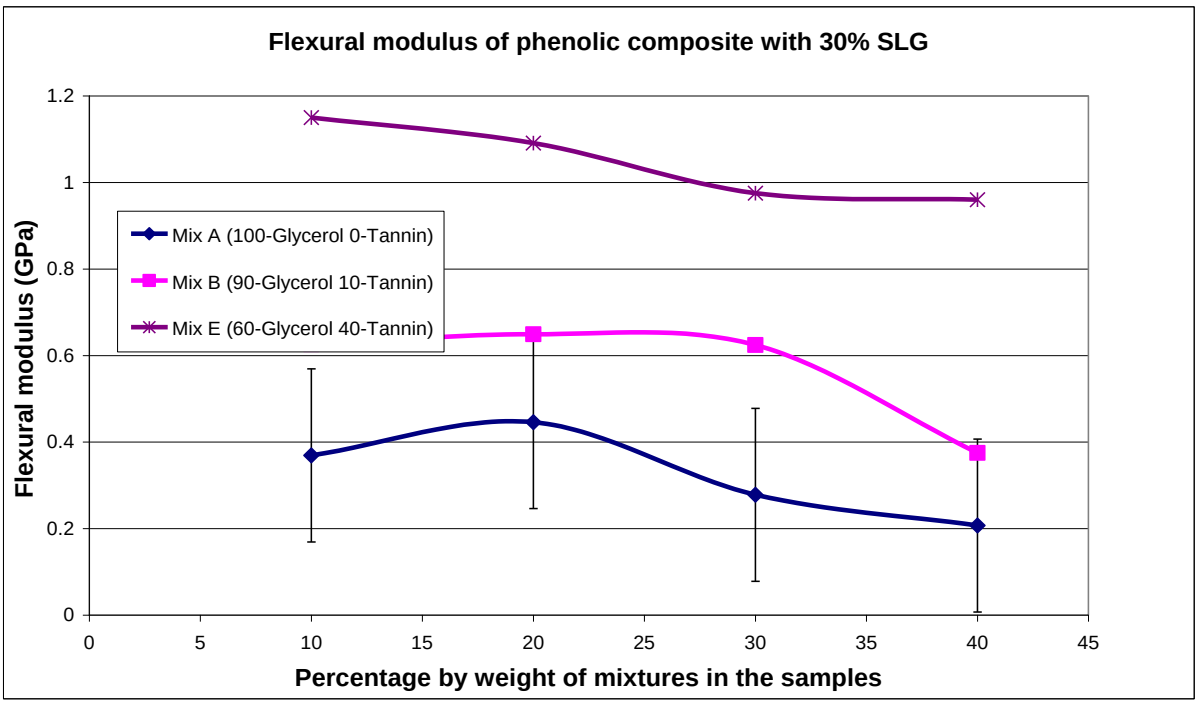

Figure 11: Flexural modulus of phenolic composite with 30% SLG

Table 1: Proportions of the 16 samples for the Mix C

Phenolic resin (g)	Mix C (g)	Slg (g)	Phencat 15 (g)	Aerosil (g)
90	10	/	5	/
80	20	/	7	/
70	30	/	8	/
60	40	/	10	/
90	10	20	7	2
80	20	20	9	2
70	30	20	10	2
60	40	20	12	2
90	10	30	7	1
80	20	30	9	1
70	30	30	10	1
60	40	30	12	1
90	10	40	7	1
80	20	40	9	1
70	30	40	10	1
60	40	40	12	1

Table 2: Composition of Phencat 15

Name	**%**
Xylenesulfonic acid	70-90
Phosphoric acid	10-20
Water	1-10

Table 3: Composition of Borden Cellobond J2027L

Name	**%**
Phenol/formaldehyde resin	30-60
Phenol	1-10
Formaldehyde	1-5
Water	10-12

Table 4: Composition in mass (g) of each mix

	Glycerol	Tannin	Sulphuric acid
Mix A (100-0)	700	0	0
Mix B (90-10)	630	70	7
Mix C (80-20)	560	140	7
Mix D (70-30)	490	210	7
Mix E (60-40)	420	280	7